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HON. T. A. CRERAR, MINISTER; CHARLES CAMSELL, DEPUTY MINISTER

MINES AND GEOLOGY BRANCH
JOHN MCLEISH, DIRECTOR

BUREAU OF MINES
W. B. TIMM, CHIEF

IMPROVING THE PROPERTIES OF CLAYS AND SHALES

BY
J. G. Phillips

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Improving the Properties of Clays and Shales

INTRODUCTION

Throughout Canada the greater part of the surface (overlying the bed rock) is the result of, or has been subjected to extreme glaciation, which accounts for the heterogeneous character of the soil mantle, and the nature of the clay deposits. The clays were mostly deposited from the waters of melting, receding glaciers, which left gravel, sand, silts, boulder clays, stoneless clays, and highly colloidal clays, depending upon the conditions under which the waters laid down their burden of suspended material. For a detailed treatise upon the geology of Canadian clays, and detailed descriptions of the deposits in the different provinces, reference may be made to the reports of J. Keele and H. Ries.[1]

Clays may be divided generally into high-grade and low-grade clays. To the first class belong the china clays, fireclays, and some of the pottery clays. The second class embraces all of the impure clays such as are generally used in the manufacture of sewer pipe, brick, building tile, roofing tile, and other types of "heavy clay products." Only a few clay deposits in Canada may properly be placed in the first class, and most of these deposits are remote from the more populated areas. Therefore, only the lower grade clays are dealt with in this report, and the problems to be considered relate to the use of this type of clay in the manufacture of clay products.

The low-grade clays vary widely in their properties and in the uses for which they are suited. In this class the best are those capable of being vitrified. To come within this category a clay must approach vitrification gradually, which implies that the impurities are so proportioned that with an increase in temperature a gradual and progressive increase in their fluxing action takes place. This gives a long burning range and permits the formed clay being fired to a high degree of density without appreciable danger of the ware becoming overfired.

Lime in appreciable quantity is an impurity harmful to the burning properties of clays. It is a very active flux but it forms sharp eutectics with most of the other minerals present in clay. Consequently after a temperature is reached at which it begins to flux there is little margin between that temperature and the fusion temperature of the entire mass. For this reason, it is difficult and often dangerous to carry high-lime clays to a high degree of density, that is, they are not good vitrifying

[1] Ries, Heinrich, and Keele, Joseph: "Clay and Shale Deposits of Nova Scotia and Portions of New Brunswick," Geol. Surv., Dept. of Mines, Canada, Mem. 16E, (1911).
Ries, Heinrich, and Keele, Joseph: Report on the Clay and Shale Deposits of the Western Provinces. Geol. Surv., Dept. of Mines, Canada, Mem. 24E, (1912).
Ries, Heinrich, and Keele, Joseph: Report on the Clay and Shale Deposits of the Western Provinces, Part II. Geol. Surv., Dept. of Mines, Canada, Mem. 25. (1913).
Keele, Joseph: "Clay and Shale Deposits of New Brunswick." Geol. Surv., Dept. of Mines, Canada, Mem. 44, (1914).
Ries, Heinrich: "Report on the Clay and Shale Deposits of the Western Provinces," Part III. Geol. Surv., Dept. of Mines, Canada, Mem. 47, (1914).
Keele, Joseph: "Preliminary Report on the Clay and Shale Deposits of the Province of Quebec," Geol. Surv., Dept. of Mines, Canada, Mem. 64, (1915).
Ries, Heinrich: "Report on the Clay and Shale Deposits of the Western Provinces," Part IV. Geol. Surv., Dept. of Mines, Canada, Mem. 65, (1915).
Keele, Joseph: "Report on the Clay and Shale Deposits of the Western Provinces," Part V. Geol. Surv., Dept. of Mines, Canada, Mem. 66, (1915).
Keele, Joseph: "Preliminary Report on the Clay and Shale Deposits of Ontario." Geol. Surv., Dept. of Mines, Canada, Mem. 142, (1924).

clays. Lime also counteracts the effect of iron oxide toward developing a red colour, and if present in considerable amounts it bleaches the fired colour to either a buff or an unfavourable salmon. For further information relative to the effect of lime and other fluxing impurities on the firing properties of clays, references are given below.[1]

Most of the low-grade clays of Canada available to the manufacturer of clay products contain lime.

In the Maritime Provinces clays free from lime are to be found, but in Quebec, Ontario, and the greater part of the western provinces, almost all the clays available to the manufacturer of heavy clay products contain appreciable quantities of lime. In Quebec and Ontario are a number of localities where clays are found with a content of lime sufficiently low to permit them to be fired to a good red colour and a good degree of density. These may be used for the production of good quality red face brick, but they cannot be considered good vitrifiable clays. A few have been used for the production of sewer pipe, but considerable care in firing is necessary, because of the amount of lime they contain. Some clays in Quebec and, to a lesser extent in Ontario, are of a highly colloidal nature, which gives rise to difficulty in drying. Not only has the loss from cracking to be contended with, but there is involved the added expense of a long drying time. Fortunately, however, in Quebec and Ontario, the best brick clays are near the more thickly populated centres.

Most of the clays available to the manufacturer of clay products in the Prairie Provinces are unconsolidated surface clays of glacial origin, having certain characteristics in common; all are more or less calcareous, and many are silty. Shales of Cretaceous and Tertiary age are to be found, but they are commonly so covered with overburden as to be inaccessible. Outcrops are available in some districts along the banks of streams, in valleys, or along the escarpments of uplands, but the better type of shales, as regards content of lime, working properties, fired colour, and firing properties, have a tendency to crack so severely during drying that their use for the production of structural clay products was almost abandoned for some years. In general, then, the practice in the Prairie Provinces with regard to the raw materials for the production of structural clay products has been either to use the calcareous highly impure surface clays, or to attempt to overcome the difficulties met with in the use of the purer, but extremely tender-drying shale.

It is evident from the foregoing then, that the manufacturer of clay products in Canada is not in a position to be too discriminating in his choice of raw materials. He must select the best available, and then adjust his methods of processing so as to obtain the best results possible. The development of new methods of treating or processing clays to enhance their properties or to improve the finished ware made from them must necessarily benefit the clay products industry.

The present report covers the results of the work carried out with this objective in the Ceramics Laboratories of the Department of Mines and Resources, and in it are incorporated results obtained elsewhere which are considered of possible value to the clay worker.

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[1] Ries, H.: "Clays, Their Occurrence, Properties and Uses." John Wiley and Sons, Inc., New York.
Wilson, H.: "Ceramics—Clay Technology." McGraw-Hill Book Co., Inc., New York.

CHAPTER I

TREATMENT OF TENDER-DRYING CLAYS TO OVERCOME DRYING DIFFICULTIES

In 1926 a request came from several manufacturers of clay products in the Prairie Provinces for assistance in overcoming difficulties in the drying of certain clays and shales for the production of structural clay products. The problem was taken up by what was then the Ceramics Division of the Department of Mines of Canada, and several reports and papers covering the results of the work have since been published.[1] In the present chapter this work is reviewed and incorporated with information obtained subsequently.

The drying problem has been more acute in the Prairie Provinces than in other parts of the Dominion, although trouble from this cause has been encountered in the east.

Professor W. G. Worcester, in his very thorough investigation of the clays and shales of Turner Valley, Alberta,[2] found certain good, red-burning clays possessing normal drying characteristics. Otherwise, it may be said, in general, that throughout the Prairie Provinces, to obtain red-burning clays possessing good firing properties, it is necessary to resort to the tender-drying shales. Common brick (made by either the stiff-mud or the soft-mud process) and tile of satisfactory quality are made from the glacial surface clays. Buff, brown, and grey face brick of high grade are made at Claybank, Saskatchewan, from the less refractory clays taken from the Whitemud beds in southern Saskatchewan. In Winnipeg the only local face brick available to builders are made from glacial clays. One such clay is the gumbo clay, from glacial Lake Agassiz, mixed with the surface clay overlying it. This gumbo clay is highly colloidal; when wet it is very sticky and gives rise to serious drying troubles. Bricks made from this mixture were of decidedly inferior quality as regards colour, strength, and density. Bricks made from the gumbo clay alone could not be dried without warping and extreme cracking. The gumbo had to be loaded with the limy surface clay and sand, and even then considerable cracking took place. This constituted one of the first drying problems presented.

In Saskatchewan, clays that can be burned to a good red colour are also rare. One clay-shale, available in abundance near Estevan, Saskatchewan, fires to a fine cherry red colour. Its other firing properties are also

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[1] Fréchette, Howells, and Phillips, J. G.: "An Investigation on the Treatment of Certain Western Clays to Overcome Drying Defects"; Mines Branch, Dept. of Mines, Canada, Rept. 697, p. 4 (1927).
Phillips, J. G.: "The Continuation of the Investigation of the Treatment of Clays to Overcome Drying Defects"; Mines Branch, Dept. of Mines, Canada, Report 722, p. 46 (1928-29).
Phillips, J. G.: "The Continuation of the Investigation of the Treatment of Clays to Overcome Drying Defects"; Mines Branch, Dept. of Mines, Canada, Report 726, p. 75 (1930-31).

[2] Worcester, W. G.; "The Clay and Shale Resources of Turner Valley and Nearby Districts"; Mines Branch, Dept. of Mines, Canada, Rep. 729 (1932).

good, but it possesses an extreme tendency to crack during drying, it being almost impossible to dry it intact however carefully and slowly the drying is carried out.[1]

In Alberta, aside from the glacial surface clays, the shales of the Belly River formation are almost the only red-burning material with good firing properties available to the brick manufacturer. These also possess decided tendencies to crack during drying from the plastic state. For years brick manufacturers struggled to make brick and tile from these tender-drying shales, usually mixed with the overlying surface clays, which also possessed tendencies to crack, but to a smaller degree. Even with the addition of sand it was extremely difficult to dry the ware without cracking.

REVIEW OF LITERATURE ON TREATMENT OF CLAYS TO IMPROVE THEIR DRYING PROPERTIES

Edward Orton, Jr.[2] was probably the first to study the tender-drying western clays and shales and to investigate possible means of remedying their drying defects. He concluded that the preheating method, introduced by A. V. Bleininger[3] when working with an Illinois joint clay, a few years previously, was the only remedy. Joseph Keele[4] followed up the work and experimented also with coagulating chemicals. Of the chemicals tried sodium chloride gave the most promise, but the improvement was not sufficient to permit large size brick and tile made from these clays to be safely dried. He also concluded that preheating was the most promising method of treatment.

N. B. Davis[5] a few years later experimented with the use of lime on clays having excessive cracking characteristics. Hydrated lime had been used for many years by agriculturists as a means of quickly granulating a heavy sticky soil. Lime is not a coagulating chemical but as most clays, particularly highly colloidal clays, contain appreciable amounts of silicic acid and its salts in colloidal gelatinous form, the reaction of lime forms a new chemical arrangement which brings about a physical change in the colloidal part of the clay. Davis found that the amount of lime required varied with the type of clay used, but when added in the proper amount the cracking tendency would disappear. For the production of common ware (in which good colour and high density are not of prime importance) the use of lime is satisfactory, providing too much of it is not required. However, in the case of the better grades of clay products (face brick, etc.) the effect on burned colour and firing properties would be objectionable.

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[1] Ries, Heinrich, and Keele, Joseph: "The Clay and Shale Deposits of the Western Provinces," Geol. Surv., Dept. of Mines, Canada, Mem. 24E, p. 80 (1912).

[2] Orton, Edward, Jr.: "Experiments on the Drying of Certain Tertiary Clays," Trans. Amer. Cer. Soc., 13, 781 (1911).

[3] Bleininger, A. V.: "The Effect of Preliminary Heat Treatment Upon Clays," Trans. Amer. Cer. Soc., 11, 392 (1909).

[4] Keele, Joseph: "Drying Defects in Some Cretaceous Clays of the Great Plains Region of Canada"; Trans. Amer. Cer. Soc., 114, 152 (1912).

Keele, Joseph: "Experiments in Preheating Clays, Report on Clay and Shale Deposits of the Western Provinces"; Geol. Surv., Dept. of Mines, Canada, Mem. 25, p. 83 (1913).

[5] Davis, N. B.: "The Effect of Lime on Certain Cracking Clays;" Trans. Amer. Cer. Soc., 17, 497 (1915).

Elsewhere, a number of investigators have studied the effect of coagulants on the properties of clays or shales. Bleininger[1] and Fulton, working with a Georgia kaolin, found that both hydrochloric and sulphuric acids produced a decided increase in shrinkage on drying.

Homer F. Staley[2] obtained beneficial results from the use of sodium chloride on an Iowa loess clay, but clays of this kind are not comparable in drying characteristics to the highly plastic western clays. Later, H. G. Schurecht[3] found that sulphuric acid when added to a Kentucky ball clay in the same proportions as used by Bleininger and Fulton produced an increase in the drying shrinkage. Kerr and Fulton[4] experimented with the chlorides of sodium, calcium, barium, and aluminium, and found that a considerable variation in volume drying shrinkage resulted from additions of these electrolytes to a ball clay and a fireclay. Back,[5] working with a North Carolina kaolin, a Georgia kaolin, and a Tennessee ball clay, found that neutral salts as well as acids and alkalis have a decided influence on the shrinkage and viscosity of clays. His work led him to the opinion that the coagulating power of neutral salts and also the rapidity of coagulation increased with their valency.

From the work of these early investigators, it is apparent that the results are not in agreement as to the coagulating power of the various electrolytes studied, and that different clays respond differently to treatment with various electrolytes.

In recent years a number of investigators[6] have again taken up the study of the effect of electrolytes in altering the properties of clays. Some have investigated primarily their effect in improving working properties and dry strength, others have sought improved methods of treatment to overcome drying troubles.

CLAYS SELECTED FOR STUDY

Most of the drying investigation was carried out on five clays or shales designated here by the letters A, A-1, B, C, and D.

A represents the kind abundant in the vicinity of Redcliff, Alberta, which has been used extensively for the production of various structural

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[1] Bleininger, A. V., and Fulton, C. E.; "The Effect of Acids and Alkalies upon Clays;" Trans. Amer. Cer. Soc., 14, 827 (1912).

[2] Staley, Homer F.; "The Effect of Salts on the Drying Behaviour of Some Clays;" Trans Amer. Cer. Soc., 17, 697 (1915).

[3] Schurecht, H. G.: "The Effect of Electrolytes on Some Properties of Clays;" Jour. Amer. Cer. Soc., 1, 201 (1918).

[4] Kerr, C. H., and Fulton, C. E.: "The Effect of Some Electrolytes on Typical Clays;" Trans. Amer. Cer. Soc., 15, 184 (1913).

[5] Back, R.: "The Effect of Some Electrolytes on Clay;" Jour. Amer. Cer. Soc., 16, 515 (1914).

[6] Fréchette, Howells, and Phillips, J. G.: "Correction of an Extreme Case of Cracking in the Drying of Brick;" Jour. Amer. Cer. Soc., 12, 153 (1929).

Phillips, J. G.: "A New Method of Treating Clays to Overcome Drying Defects;" Trans. Can. Inst. of Min. and Met., 32, 270 (1929).

Husain, T.: "Altering the Properties of Clays by the Use of Electrolytes;" Jour. Amer. Cer. Soc., 13, 805 (1930).

Simpson, H. E.: "Correcting a Tender Shale;" Jour. Amer. Cer. Soc., 13, 817 (1930).

Bangs, W. C. and Greaves-Walker, A. F.: "Working Unworkable Shales by the Use of Acids;" North Carolina State College of Agriculture and Engineering.

Clews, F. H.: "Conditioning of Clay in the Plastic State;" Trans. of the Cer. Soc. (English) 33, (1), 1 (1934).

Macey, H. H.: "The Promotion of the Drying of Clay by the Coagulating Effect of Acid;" Trans. of the Cer. Soc. (English) 39, (9), 396 (1935).

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clay products. It belongs to the Belly River formation, and a section of the bank from which the material studied was taken is as follows:

First 2 feet.	Sandy, buff-burning clay containing limestone pebbles.
2 to 4 feet.	Buff-burning clay containing less sand and fewer limestone pebbles than the above.
4 to 20 feet.	Red-burning, tender-drying clay containing much sand.
20 to 50 feet.	Very plastic shale—used in making stiff-mud and pressed brick—shale-clay A.

A-1 is similar to A, but was taken from a deposit in Medicine Hat. It has been used for years in the production of brick and tile. As taken from the bank it has much sandy clay and surface clay mixed in it, yet it presents serious drying troubles.

B came from a point about one and one-half miles east of Estevan, Saskatchewan. A section there shows:—

10 to 20 feet.	Boulder clay.
8 feet.	Lignite.
2 feet.	Parting clay.
8 inches to 2 feet.	Lignite.
30 to 40 feet.	Blue shale clay (shale-clay B).

C represents the gumbo clay from glacial Lake Agassiz that underlies from 4 to 5 feet of surface clay in the vicinity of Winnipeg, Manitoba. This material is extensively distributed and has a thickness of from 30 to 40 feet. For production of brick and tile it is mixed with the upper surface clay and sand.

D represents one of the most troublesome tender-drying clays found in the east. It came from a deposit at Lakeside, about 18 miles from Montreal, P.Q. It has been used industrially chiefly for the production of hollow building tile. The pit shows 8 to 12 feet of brownish clay overlying blue-grey clay, the brown clay being merely the weathered portion of the deposit. The material from this entire section is extremely fine-grained (colloidal) and presents difficulties when being dried from the plastic state.

These five clays are considered representative of the most troublesome drying clays in Canada, the tendency to crack in clays A, B, and C being probably more severe than in any other clays worked industrially anywhere. Were it not for the fact that good clays are scarce, the working of these materials would not likely be attempted.

PREHEATING

Drying troubles met with in most of the clays worked industrially can usually be overcome by a humidity drying treatment or by the addition of non-plastics. However, for a humidity drying treatment the care and control necessary make such a method impracticable.

Results of the early investigators indicated that tender-drying clays could be dried safely by preheating. Preheating, however, would entail a high initial cost, and as it had been shown that a comparatively narrow margin separated the temperature at which the clay was rendered dryable from the overheating temperature, doubt arose as to the practicability

of the process. Brick manufacturers, at least, were not willing to risk the expense entailed in trying the process on an industrial scale.

Early in the investigations made by the Department of Mines and Resources laboratory preheating experiments were again tried. All the materials responded to the treatment, and in all cases the temperature range within which preheating gave successful results was between 450° and 550° C. In Bleininger's work the clays studied responded at temperatures considerably lower than this.

As large-scale preheating tests were precluded it was decided in the early stages of the investigation to see if a treatment with coagulating chemicals could be devised that would successfully overcome the drying difficulty. A chemical treatment offers the attractive advantage of small initial cost. A long series of tests was accordingly undertaken, in which all likely chemicals were tried, with and without the addition of non-plastics. The details are given in the reports already referred to, and only the pertinent results will be given here.

CHEMICAL TREATMENT

The most effective coagulants were found to be hydrochloric acid, sulphuric acid, and ferric chloride. Ferric chloride was by far the most effective salt in reducing the tendency of the clays to crack. In the early tests the clay was treated simply by adding different proportions of the chemicals, it was moulded into bricks (of approximately standard building brick dimensions), which were dried at 65° C., and any changes in cracking tendencies produced were observed. The three chemicals produced such marked improvement in drying behaviour that it was thought that with the addition of a small proportion of non-plastic (grog), treatment with one of these chemicals might enable the ware to be safely dried at a reasonable rate.

PLANT TEST AT REDCLIFF, ALBERTA

For the Redcliff and Medicine Hat clays, ferric chloride seemed to be even more effective in improving the drying properties than the acids. Sodium chloride, although not an effective coagulant, lowers vapour pressure and thus retards the rate of evaporation of the water. Sodium chloride alone acts as a coagulant, if enough be added, but the amount required would be harmful to the firing properties of the clays. In the plant tests, trials were made using ferric chloride alone and ferric chloride plus sodium chloride to see if by the reduction in vapour pressure brought about by sodium chloride, used in conjunction with ferric chloride, the amount of the more expensive ferric chloride required might be reduced.

A number of plant tests were made, using the two salts, and when the first tests gave favourable results the dryers were speeded up gradually so as to give faster drying rates. The following is a summary of the results obtained:

1. Ferric chloride not only rendered the clay safely dryable, but the drying period could be reduced to less than one-half.

Phillips, J. G.: "The Continuation of the Investigation of the Treatment of Clays to Overcome Drying Defects;" Mines Branch, Dept. of Mines, Canada, Rept. No. 722, p. 46 (1928–29).

2. The addition of a small amount of sodium chloride reduced the amount of ferric chloride required.

3. The optimum additions of the two salts were finally determined to be:

1·0 per cent of ferric chloride
0·5 per cent of sodium chloride
} on the basis of the weight of dry clay.

4. The amount of grog needed was not more than 10 per cent (dry clay basis); considerably less than had been expected.

5. The ferric chloride must be added in the tempering water as, being deliquescent, it will not stay as a powder, and cannot be well distributed in the dry condition.

6. Wooden tanks for the solution of the salts and acid-resisting piping and fixtures leading to the pug-mill are necessary, as ferric chloride in solution is corrosive to metal parts. After being added to the clays it was apparently not corrosive to the machine parts.

Following the successful tests, the process was immediately introduced in the plant where the tests were made. Experience in regular production over a period of six months brought forth the following facts:

The cost of the treatment, including added labour, upkeep of additional equipment, and cost of chemicals, was about $3 per thousand brick. The drying operation, which formerly required seven or eight days was reduced to three, and the drier loss was reduced from 40 per cent and more to almost nothing. The treatment resulted in an increase of output of from 24,000 to 40,000 brick per day. The treatment improved the fired colour and the general quality of the ware, as it permitted the use of a much larger proportion of the very tender underlying shale, which contains much less harmful impurities than the surface clays. The addition of the salts prevented scum, and the "popping" of limestone pebbles.

CHAPTER II

LABORATORY STUDY OF EFFECT OF CHEMICALS ON DRYING PROPERTIES OF CLAYS

Following the successful plant tests of the use of ferric chloride and sodium chloride in overcoming the drying defects of the Redcliff, Alberta, clay, the drying properties of these clays were investigated more thoroughly in the laboratory. A more precise means of measuring the effectiveness of various chemicals toward improving the drying properties of clays became imperative. Settling tests measured the coagulating power of chemicals on clays in aqueous suspension, but clay in a stiff plastic state presents a very different set of conditions, and different clays respond differently to treatment with various electrolytes.

The tender-drying clays studied in this investigation are characterized in drying by a peculiar form of cracking. Many clays crack because of an abnormally high drying shrinkage, or a too rapid rate of shrinkage. It was found that the clays under investigation owing to their colloidal make-up, crack during drying because of a relative impermeability to water. As water evaporates from the outer shell of the formed piece the movement of water from the interior is retarded by the impervious structure of the mass. The surface shell becomes quickly almost bone dry, while the interior retains much of its original water content, and consequently a characteristic form of extreme cracking is set up. High shrinkage or a too rapid rate of shrinkage usually results in the development of a few long, rather deep cracks, but this particular form is characterized by innumerable cracks running in all directions and on all sides of the ware. The drying problem, therefore, resolved itself into finding a means of opening up the structure of the clay mass so that the moisture could have more easy access to the surface.

It was thought that the determination of the moisture gradient from surface to the interior (at the critical stage of drying) of test pieces, treated and untreated, would measure the effectiveness of the treatment. After a number of trials to determine the drying temperature and the time required to bring the test pieces to the critical stage, the following procedure was followed. Test pieces in the form of cubes 2 inches square were used. Trials showed that drying the untreated cubes for three hours at 65° C. carried the drying process to the beginning of the critical stage, when the test pieces had not cracked so as to interfere with the test procedure. In order to be sure that the results were comparable, the sets of test pieces (treated and untreated) were all dried at the same time under the same conditions. After the cubes were taken from the dryer, a core one-half inch in diameter was cut from the partly dried test piece, and then beginning at the surface end of the core, successive sections were cut about 0·15 of an inch in thickness. These sections were placed in previously weighed, stoppered weighing-bottles, and the weight was taken,

after which the stoppers were removed and the clay sections allowed to dry to constant weight at 110° C. The dried weights were taken, and the percentage of moisture in each section was calculated.

Tests were carried out in this manner on a clay known to possess very good drying properties and on all the tender-drying clays under investigation, with the exception of clay C (the Winnipeg gumbo). This clay did not respond sufficiently to chemical treatment and even after treatment could not be safely dried unless a large proportion of grog was incorporated into it. Preheating is probably the only effective means of solving the drying troubles of this clay. In addition, the same test was applied to the tender-drying clay both before and after treatment with various selected chemicals. In Figures 1 to 10 are given the curves plotted from the results obtained. Hydrogen-ion concentration determinations were made on several clays (untreated and with additions of electrolytes) and the results are given in Tables I to IV.

DISCUSSION OF RESULTS

The marked divergence of the curve of the clay with good drying properties from that obtained from the tender-drying clays can be seen at a glance. It is apparent that the shape of the curve is the important criterion; it is not necessary that the moisture gradient determinations be made under exactly the same conditions of drying. Even under different conditions of drying and at different drying rates the curves obtained would be similar and would allow comparison.

The curves obtained from clays A (the Redcliff shale clay) and B (the Estevan shale clay) show the extreme degree of resistance to movement of moisture during drying, possessed by these clays when compared to the curve obtained from the good drying clay. Clay B possesses this defect to even a greater degree than clay A. When these clays are dried the water at the surface evaporates and an impervious skin is formed at the surface. The water in the interior (from a point only a short distance from the surface) is held so tightly that very little of it moves toward the surface. In a short time the surface becomes almost bone dry while the interior has retained almost all of its original water content; the large differential shrinkage results in exaggerated cracking. The total drying shrinkages of these clays are large but not abnormal; their drying defects are due solely to their peculiar behaviour with regard to movement of moisture to the surface as drying proceeds. The application of humidity drying to such clays would not be practicable, no matter how carefully controlled, and the addition of non-plastics only exaggerates the trouble. The marked improvement (as shown by the flattening out of the curves) resulting from additions of ferric chloride and hydrochloric acid is shown in Figures 7, 8, 9, and 10. Although the additions of 1·0 per cent of ferric chloride and 1·0 per cent of hydrochloric acid do not give a straight line curve, the results show improvement enough to suggest that with a reasonable amount of care safe drying can be accomplished.

Figure 4 shows the moisture-gradient curves of a Medicine Hat clay (A-1) that has been used industrially for the production of structural clay

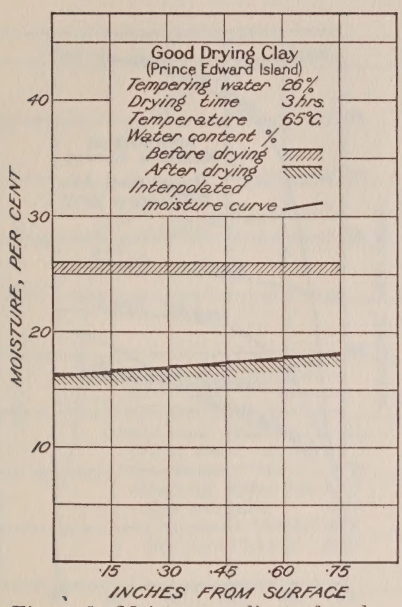

Figure 1. Moisture-gradient of a clay possessing very good drying properties. The curve is a straight line and the slope is gradual.

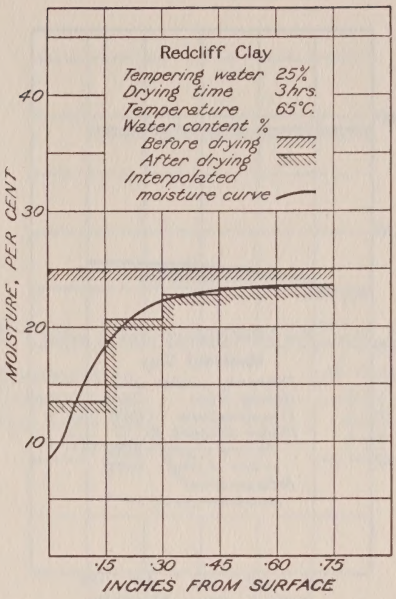

Figure 2. Moisture-gradient of a clay (shale clay A) having very abnormal drying properties.

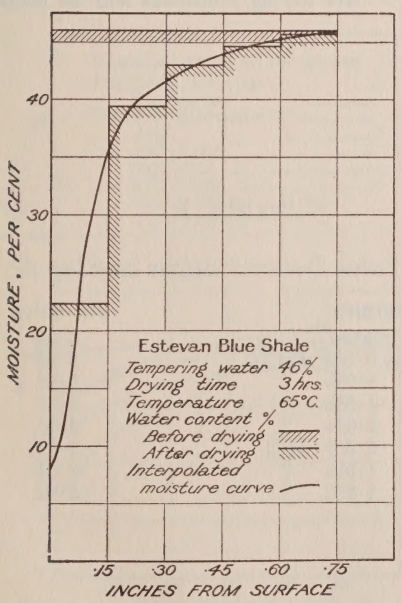

Figure 3. Moisture-gradient of a clay (shale clay B) having exceptionally abnormal drying properties. Although a large amount of water has evaporated at the surface, the original water content still remains at the centre of the piece.

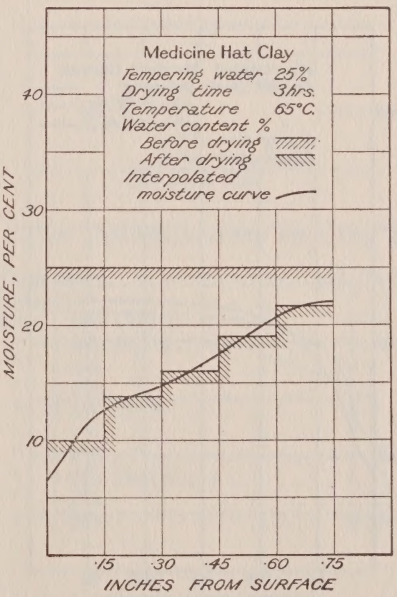

Figure 4. Moisture-gradient of a clay (clay A-1) having abnormal drying properties. It is evident that it is not nearly so resistant to movement of moisture as the clays from which the curves in Figures 2 and 3 were obtained.

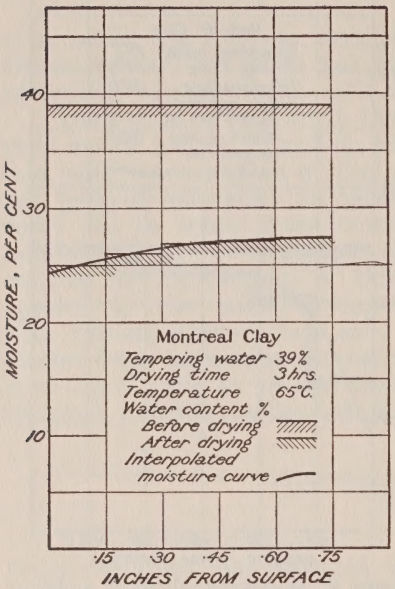

Figure 5. Moisture-gradient of a clay (clay D) having only slightly poorer drying qualities than that of a good drying clay.

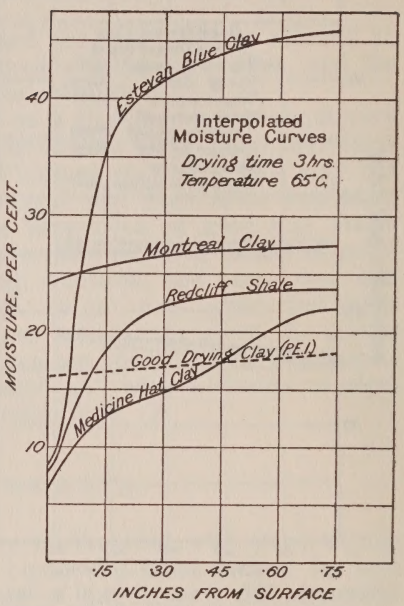

Figure 6. Moisture-gradient curves of the five clays tested are consolidated so that a comparison of the respective drying properties may be made.

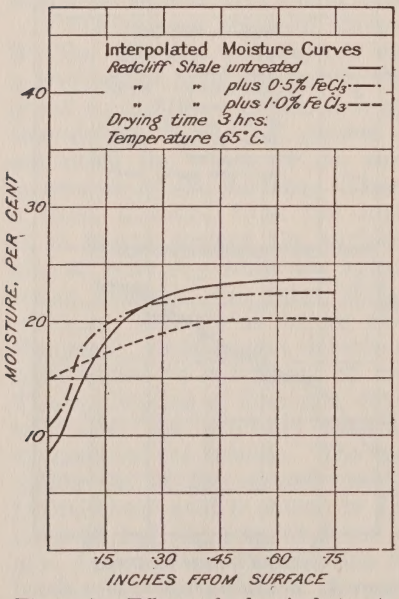

Figure 7. Effect of chemical treatment on moisture-gradient curves of clay A (Redcliff shale clay).

TABLE I

pH Value Determinations on Clay A

Treatment	pH Value
Untreated	8·65
Plus 0·5% $FeCl_3$	6·62
" 1·0% "	5·86
" 1·5% "	4·85
" 2·0% "	4·40
" 0·5% HCl	6·72
" 1·0% "	6·24
" 1·5% "	5·92

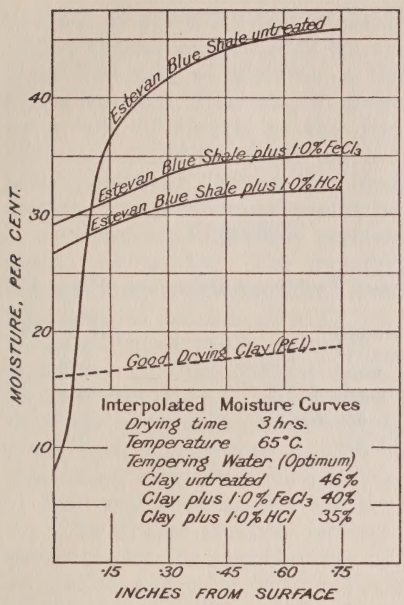

Figure 8. Effect of chemical treatment on moisture-gradient of clay B (Estevan blue shale).

TABLE II

pH Value Determinations on Clay B

Treatment	pH Value
Untreated	8·34
Plus 1·0% HCl	4·62
" 1·0% $FeCl_3$	4·81

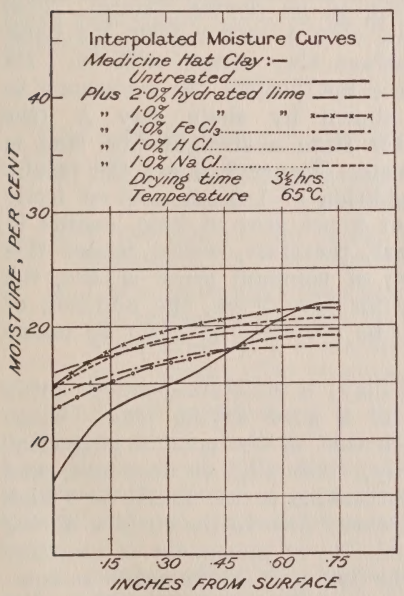

Figure 9. Effect of chemical treatment on moisture-gradient of clay A-1 (Medicine Hat clay).

TABLE III

pH Value Determinations on Clay A-1

Treatment	pH Value
Untreated	7·85
Plus 1·0% CaO	9·+
" 0·5% $FeCl_3$	6.85
" 1·0% "	6·6
" 1·5% "	6·4
" 0·5% HCl	6·9
" 1·0% "	6·8
" 1·5% "	6·73
" 0·5% $Fe_2(SO_4)_3$	6·87
" 1·0% "	6·57
" 1·5% "	6·28

64600—4½

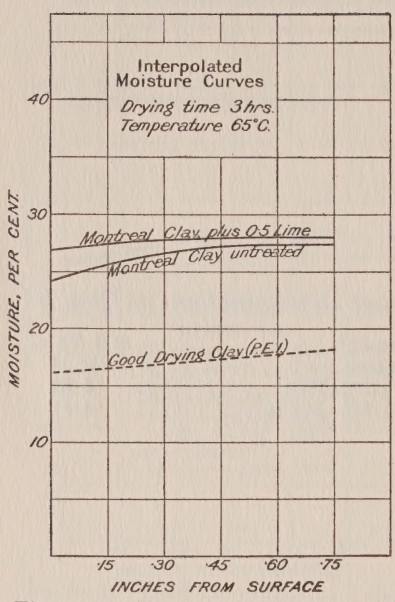

Figure 10. Effect of chemical treatment on moisture-gradient of clay D (Montreal clay).

TABLE IV

pH Value Determinations on Clay D

Treatment	pH Value
Untreated	7·70
Plus 1·0% NaCl	7·67
" 1·0% $FeCl_3$	6·67
" 0·5% CaO	8·80
" 1·0% "	9·+

products with considerable difficulty owing to its drying defects. This clay, although similar to the Redcliff shale clay, as taken from the bank has much sandy material and upper surface clay mixed with it. Its moisture-gradient curve shows that it does not possess the resistance to movement of moisture during drying shown by shale clay A (the Redcliff clay). Its curve, however, is far from a straight line, and is steep, which indicates serious drying defects. Figure 9 shows the results obtained after various treatments; the addition of 1·0 per cent of ferric chloride or hydrochloric acid, and also of 2 per cent of lime, results in a marked improvement. Either treatment, therefore, would render this clay safely dryable. For the production of common brick or tile, the addition of lime is to be recommended; for face brick, the addition of ferric chloride or hydrochloric acid is to be preferred in order to maintain a good fired colour.

In the case of clay D (the Montreal clay) a moisture-gradient curve was obtained differing little from that of a good drying clay. From a comparison of the curve of clay D with that of the good drying clay, it should not be expected to crack badly. Actually, it does not, and although it presents drying difficulties, the cracking is due chiefly to a high drying-shrinkage rather than to restricted water flow to the surface during drying. In this clay there is a slight restriction of movement of moisture shown by the slightly more rapid rise of the first part of the curve as compared to the portion representing the interior of the test piece. This clay could be remedied by using some means of reducing shrinkage or by some form of humidity-drying. This clay has been used industrially for a

number of years for the production of hollow building tile, and sawdust is added (about 30 per cent by volume) for the dual purpose of preventing drier loss and of yielding a light-weight unit. Even with the addition of the sawdust, there was, at times, a heavy drier loss from cracking, caused by a lack of control of the drying process. By the addition of sawdust the ware could be dried safely if the process were not too rapid. This plant, however, lacked the facilities for accurate control of the rate of drying, which at times would be too rapid, and the ware cracked.

In order to afford a greater margin of safety a mild chemical treatment was sought. The moisture-gradient curve in Figure 10 shows the improvement resulting from a small addition of lime. The effect of small additions of sodium chloride on the shape of the moisture-gradient curve was not measurable although it did retard the rate of evaporation of moisture. Sodium chloride does, perhaps, change to some extent the movement of moisture to the surface during drying, but the change is so small that this method is not sufficiently accurate to measure the small variation. A mixture of lime and sodium chloride was first tried at the plant, but it was found later that the salt was unnecessary and a 0·5 per cent addition of lime was adopted for regular operation.

The drying troubles arising from the use of this clay could have been overcome by the introduction of a humidity-drying process, or a carefully controlled and mild drying treatment, but the former was too costly, and in the dryers with which the plant was equipped it was impossible to maintain sufficiently accurate control to assure the mild drying treatment required. It was necessary to resort to other means, and a small amount of sodium chloride, lime, or a mixture of the two, was found to alter the clays sufficiently for it to be dried safely under the conditions prevailing at the plant.

SUMMARY AND CONCLUSIONS

As regards drying properties, clays may be divided into three classes:

1. Clays possessing satisfactory drying properties that can be dried at a moderately rapid rate without cracking.
2. Clays that exhibit a high drying shrinkage, which causes cracks to develop if they are not dried carefully.
3. Clays possessing the quality of resisting the migration of water to the surface during drying, that are characterized by severe cracking when dried at a moderately rapid rate, and that cannot be safely dried except after treatment.

The method described in this report has been found useful in determining to which of these classes a clay belongs. For those of the third class (those owing their drying defects to resistance to migration of water) it furnished a means of measuring the degree to which a clay may possess this defect, and a means of measuring the effectiveness of chemical treatment.

A number of notably bad drying clays have been investigated in this manner, classified according to drying properties and, in the case of those requiring it, the kind and amount of treatment necessary to correct the defect has been determined.

Determinations of hydrogen-ion concentration are of some use for indicating the effectiveness of chemical treatment, but are not nearly so informative as the moisture-gradient curves.

Chemical treatment can be applied not only to render certain clays dryable that otherwise could not be safely dried commercially, but to less severe cases requiring a long and careful drying process to avoid a heavy drier loss in which it will (1) reduce considerably the drying time needed, thereby increasing the capacity of the plant and saving fuel; (2) reduce costs by reducing drier loss substantially; (3) improve the quality of the ware.

COMMERCIAL APPLICATION OF CHEMICAL TREATMENT

Besides the Redcliff Company, several other concerns in the vicinity of Medicine Hat, Alberta, have resorted to chemical treatment in order to utilize local clays. In Medicine Hat one company used ferric chloride for the production of face brick and lime for common brick and tile. It was reported that drying in this plant was greatly improved as a result of such treatment.

In a pottery at Medicine Hat a similar clay taken from a pit not far from the brick plant mentioned above has been used for some time for the production of red flower pots. The ability to correct the defects of the Medicine Hat clay by chemical treatment made possible the production of a good grade of flower pot from this material. The clay fires to a good red colour, and by the addition of 0·5 per cent of ferric chloride, the pots are dried safely without cracking. As the pots are dried in air at room temperature a smaller amount of ferric chloride is required than if they were dried more rapidly; the problem is further simplified by the fact that a much smaller cross-section of clay mass has to be dried than in brick or tile. Without the addition of ferric chloride the pots crack badly even when dried at this slow rate. This clay contains a quantity of soluble salts, which would cause the formation of a discolouring scum on the ware, did not the ferric chloride prevent its appearance on the fired ware; and the amount of barium carbonate required is reduced.

The Estevan clay has not as yet been worked by the stiff-mud process for the production of brick and tile, but it offers good possibilities. Given a means of counteracting its cracking tendency, it should yield a very good grade of red face brick, and materials that will yield high-grade face brick of a good red colour are rare in Saskatchewan and Manitoba. It has good working properties, a good, rather wide, firing range, and fires to a fine cherry-red colour. Although plant trials were not conducted with it, the results of the laboratory investigation, particularly the moisture-gradient curve, show that a 1·0 per cent addition of hydrochloric acid or ferric chloride, with possibly a small amount of non-plastic, would render the clay safely dryable from the stiff plastic state. It occurs in abundance, and as the market demand in the Prairie Provinces increases, this clay will become an important raw material for the production of clay products.

Attempts were made by plant trials to remedy the drying troubles arising from the use of clay C (the Winnipeg gumbo) by the addition of sodium chloride. This clay as mined is in a wet, sticky condition, and

is not dried before using, the only grinding it receives being to run it through a shredder, which merely breaks down the large lumps. Owing to its wet condition the admixture of non-plastics is difficult, a uniform distribution not being obtainable, nor can chemicals be introduced with the tempering water because very little water is added. In the plant trials the sodium chloride was fed to the regular mixture of gumbo, surface clay, and sand, before it went to the shredder. Trials were made using one, two, and three per cent of sodium chloride.

The results of the tests were not promising, as little improvement in drying resulted from adding even three per cent of sodium chloride. One reason for the failure was the inability to get the sodium chloride uniformly distributed throughout the clay. It is questionable, moreover, whether a sufficient improvement would result even if a uniform mixture of clay and salt were obtained. As mentioned previously this material did not respond, in the laboratory, to the strongest coagulating chemicals. Plant trials were made with sodium chloride with the thought in mind that the retarding effect on evaporation of moisture caused by sodium chloride might produce sufficient improvement to warrant its use. At this plant drying is done in open air racks and great difficulty is experienced in maintaining a sufficiently slow and uniform drying rate so that the bricks will not crack.

The conclusion is that the only effective means of improving the drying properties of this material would be preheating. High-grade ware of good colour, however, could not be made from it, even though its drying defects were corrected (because of its impure nature), and it is doubtful whether the expense that preheating would entail is warranted.

DRYING METHODS

The drying of clay wares is a subject that has been covered in a number of text-books, papers, and articles. There are numerous systems, ranging from open air drying to the comparatively complex, that permit an accurately controlled humidity drying treatment. The choice of the drying system depends on the kind of ware to be made as well as on the drying properties of the clay. The subject cannot be covered in this report, but in the bibliography at the end of the chapter references will be found which may be consulted for information on this subject.

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CHAPTER III

"POPPING" OF LIMESTONE PEBBLES

Many of the clays in Canada used in the manufacture of clay products contain limestone pebbles, which if in appreciable amount give rise to serious "popping" and possibly to disintegration of the ware unless preventive measures are taken. During firing the limestone is converted to quicklime, which subsequently absorbs moisture and carbon dioxide from the atmosphere. This slaking process of the quicklime is accomplished by an increase in volume, causing a disruption of the ware to an extent proportional to the size of the pebbles and the number present. Reference is made to a report[1] entitled "Utilization of Pebbly Clays for Heavy Clay Products Manufacture," by Fred T. Heath, in which is presented a review of methods devised either to clean the clays of limestone pebbles or to render them harmless. No economical process for removing pebbles completely has yet been developed. Washing and air separation are the only feasible methods by which the clay can be freed entirely from pebbles and cost has kept them from being considered as practicable for heavy clay products. The so-called clay cleaners, many forms of which have been developed, remove the pebbles only partly, but they serve a useful purpose, for the residue may be rendered harmless by fine grinding. Two methods commonly employed in the industry to remove pebbles are:

(1) The use of conical rolls of various design, which throw the larger pebbles out to the side. This method has special use when the clay is not dry.

(2) When the clay is dry and crumbles easily, raising the mullers in the dry pan so that the pebbles will not be crushed. The clay will then sift through the orifices in the bottom of the pan.

Methods available for minimizing the harmful effects of limestone pebbles may be listed as follows:

(1) Grinding them with the clay to such a degree of fineness that the expansion during slaking will not disrupt the ware.

(2) Firing the ware to a high degree of hardness.

(3) Firing under reducing conditions.

(4) Soaking the ware in water immediately after firing.

(5) The incorporation of a fluxing salt such as sodium chloride in the body before firing.

In the plant tests on the tender-drying clays it was observed that the chemicals used prevented the popping of the limestone pebbles in the brick. Joseph Keele[2] some years ago experimented with sodium chloride and

[1] Ohio State University Engineering Experiment Station, Bull. No. 59.
[2] Keele, Joseph; "Methods of Handling Brick Clays Containing Stones;" Clay Worker, Vol. 74, p. 230 (1920).

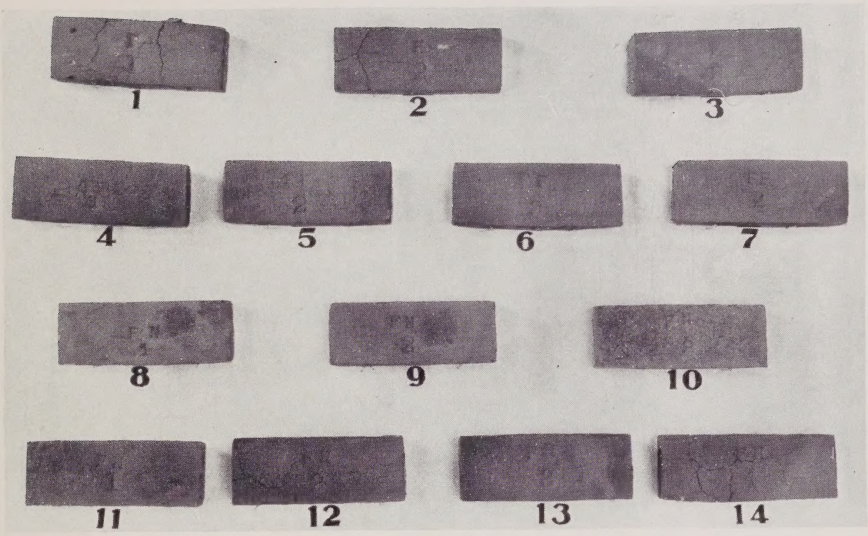
found it very effective in preventing this. Heath[1] followed up Keele's work and also tried calcium chloride, sodium sulphate, sodium bicarbonate, and sodium carbonate. He found sodium chloride to be the most effective, and following it the others in the order given. As the effect of ferric chloride and hydrochloric acid (two chemicals used in treating the tender-drying clays) on the popping of pebbles had not been investigated, the following experiment was tried to compare their effectiveness in this regard to that of sodium chloride.

A shale known to contain no lime pebbles and used industrially for the manufacture of face brick was selected for the test. It contained lime carbonate but distributed uniformly throughout the clay in a finely comminuted form. It was chosen because it does not fire to a high degree of hardness until near its fusion point. Such a material should afford better observation of popping than a clay that becomes very dense on being fired, because hard firing tends to prevent popping. Limestone pebbles were prepared by crushing ordinary limestone and screening to a —8 +12 Tyler standard sieve size. The following series of briquettes was made up:

No.	Limestone pebbles (—8 +12) added to the clay, per cent	Chemicals added
1	5	Untreated
2	7	"
3	3	"
4	5	1·0% $FeCl_3$
5	3	" "
6	7	" "
7	5	0·5% "
8	5	1·0% NaCl
9	3	" "
10	7	" "
11	5	0·5% HCl
12	7	" "
13	3	" "
14	5	1·0% "

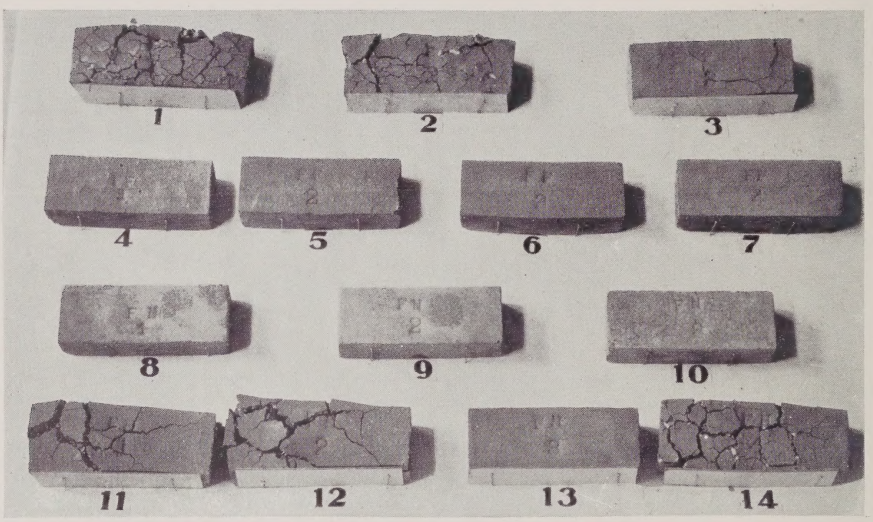
All briquettes were fired at the same time to cone 06(1841° F.), after which they were allowed to stand in air and observations were made from time to time for evidence of popping. Cracks did not appear until one month after firing, although there was evidence of incipient popping before. Plate I shows the condition of the briquettes after standing in air for one month. Plate II shows their condition after standing in air for two months. The effectiveness of both sodium chloride and ferric chloride in preventing the popping of limestone pebbles is apparent; whereas hydrochloric acid is ineffective. All untreated briquettes as well as those treated with hydrochloric acid were found to have developed cracks at the end of two months. Those briquettes with the larger amounts of pebbles (5 and 7 per cent) were disrupted by them, and after standing for four months all untreated briquettes and those treated with hydrochloric acid had completely disintegrated. Even after standing for six months none of the briquettes treated with sodium chloride showed any sign of cracking, and only one of the test pieces treated with ferric chloride showed evidence of popping—the one containing 7 per cent of — 8 + 12-mesh limestone pebbles and treated with one per cent of ferric chloride.

[1] Heath, Fred T.: Op. cit.



Effect of chemical treatment on clays containing varying amounts of limestone pebbles (−8+12 mesh). Briquettes fired to cone 06 and allowed to stand one month in air.

Specimen No.	Limestone %	Treatment		
1. . . .	5	Untreated		
2. . . .	7	"		
3. . . .	3	"		
4. . . .	5	Plus	1·0%	$FeCl_3$
5. . . .	3	"	"	"
6. . . .	7	"	"	"
7. . . .	5	"	0·5%	"
8. . . .	5	Plus	1·0%	NaCl
9. . . .	3	"	"	"
10. . . .	7	"	"	"
11. . . .	5	"	0·5%	HCl
12. . . .	7	"	"	"
13. . . .	3	"	"	"
14. . . .	5	"	1·0%	"



Same specimens as shown in Plate I after standing two months in air.

Specimen No.	Limestone %	Treatment		
1. . .	5	Untreated		
2. . .	7	"		
3. . .	3	"		
4. . .	5	Plus	1·0%	FeCl3
5. . .	3	"	"	"
6. . .	7	"	"	"
7. . .	5	"	0·5%	"
8. . .	5	Plus	1·0%	NaCl
9. . .	3	"	"	"
10. . .	7	"	"	"
11. . .	5	"	0·5%	HCl
12. . .	7	"	"	"
13. . .	3	"	"	"
14. . .	5	"	1·0%	"

CONCLUSIONS

1. Both sodium chloride and ferric chloride are effective in preventing the popping of limestone pebbles. A one per cent addition of sodium chloride is effective even with seven per cent of — 8 + 12-mesh limestone pebbles. A one per cent addition of ferric chloride is effective only up to a five per cent content of — 8 + 12-mesh pebbles.

2. Hydrochloric acid has no effect on the popping of limestone pebbles.

3. In addition to improving drying properties both sodium chloride and ferric chloride constitute a valuable ingredient in pebbly clays in that they ensure against the harmful effects resulting from pebbles left unground in the clay ware. Even though the pebbles are small enough not to cause cracks, they are sure to disfigure the surface of face bricks by the appearance of white powdery spots when they break through the surface skin of the brick.

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CHAPTER IV

IMPROVING THE WORKING AND FIRING PROPERTIES OF CLAYS AND SHALES

The investigational work covered in this chapter had for its primary objective the development of a practical means of increasing the fired density of ware made from various Canadian clays or shales.

As stated previously, owing to the limy nature of the clays common in Canada, it is usually very difficult to fire ware formed from them to a high degree of density, i.e. low absorption. In addition, many of the clays are silty and lacking in plasticity and are therefore difficult to work in the stiff plastic state, which adds to the porosity caused by the presence of lime.

Calcium carbonate in clays or shales prevents the development of a good degree of density in two ways. First, in the early stages of firing, carbon dioxide is evolved which leaves minute pores where the carbonate has been decomposed. Second, it does not flux with the other mineral components, with advancing temperature, until a point is reached that is close to the temperature of fusion of the entire mass. In order to obtain density in fired clay wares it is fundamentally important that an appreciable degree of fluxing take place between the low fusing components and between the low and high fusing components of the clay, in order to close or fill the pores. It is also equally important that the interfluxing of the components progress gradually, with advancing temperature, in order to ensure against the danger of deformation.

In considering possible means of increasing the density of the various Canadian clays under investigation, the methods of treatment may be divided into three heads:

(1) The addition of cheap, low-fusing fluxes; (2) improving the workability by chemical conditioning, thereby permitting a closer knitting together of the individual particles of the clay body; and (3) de-airing the clay in the plastic state.

Little hope was offered by the addition of fluxes, as any effective agents of this kind are much too expensive.

Chemical conditioning and de-airing or the combination of the two were thought to have possibilities. It was therefore decided to investigate these two methods of treatment thoroughly.

REVIEW OF THE LITERATURE ON THE CHEMICAL CONDITIONING OF CLAYS IN THE PLASTIC STATE

One of the first to search for a means of increasing the plasticity of certain American clays was E. G. Acheson.[1] He reported that favourable results were obtained with additions of gallotannic acid. L. H. Minton[2] followed up Acheson's work and found that the treatment did not seem to influence plasticity as much as had been reported. P. Rohland[3] observed the alteration of working properties caused by additions of small amounts of electrolytes. H. E. Ashley,[4] working with a number of English and American clays, found that clays were deflocculated by ammonia, potassium hydroxide, sodium hydroxide, sodium oxalate, potassium oxalate, ammonium oxalate, sodium silicate, soft soap, borax, potassium phosphate, potassium cyanide, potassium ferrocyanide, sodium arsenite, potassium permanganate, and sodium sulphide.

He also noted that clays were coagulated by calcium chloride, ammonium nitrate, sodium sulphate, ammonium sulphate, calcium sulphate, ferrous and ferric sulphates, lead acetate, carbonic acid, potassium di-chromate, hydrochloric acid, and ammonium, sodium, zinc, magnesium, and barium chlorides.

A. V. Bleininger and C. E. Fulton[5] studied the effect of acids and alkalis upon clay in the plastic state. They reported that the principal result of adding hydrochloric and sulphuric acids in small amounts to a Georgia kaolin in its most workable state was to reduce shrinkage.

Robert Back[6] investigated the effect of sodium, calcium, and aluminium chlorides on a kaolin from Georgia, a kaolin from North Carolina, and a ball clay from Tennessee. He reported that the flocculating power and relative coagulating speed of these salts was in the order of their valency.

J. Minnemann[7] showed that pottery scrap clay that had become deficient in plasticity through drying or other causes could be rendered more workable by the addition of acids or acid salts.

H. G. Schurecht[8] observed that the same electrolyte could behave differently in different clays.

M. Jacoby[9] reported that the plasticity of several German kaolins was reduced instead of enhanced by the addition of hydrochloric acid or common salt.

More recently W. C. Bangs[10] and Professor A. F. Greaves-Walker showed that shales previously considered unworkable could be made workable by the use of acids. Small amounts of concentrated commercial hydrochloric and sulphuric acids added to the pugging water of three shales increased their plasticity. Such treatment likewise increased the length of the bar that could be extruded from an auger machine die without breaking when supported at the free end only, increased the dry strength

[1] Acheson, E. G.: Trans. Amer. Cer. Soc., 6, 31 (1904).
[2] Minton, L. H.: Trans. Amer. Ceram. Soc., 6, 231 (1904).
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[8] Schurecht, H. G.: Trans. Amer. Ceram. Soc., 19, 120 (1917).
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[10] Bangs, W. C. and Greaves-Walker, A. F.: Ceramic Age, 20, 1, 23 (1932).

and brightened the red colour of the shale when fired to cone 02 (2003° F.). They believed that much the same result is accomplished as when clay is de-aired.

E. C. Henry[1] reported that two clays from New Brunswick, N.J., were considerably improved in plastic behaviour by the addition of one per cent of concentrated hydrochloric and sulphuric acids to the tempering water.

It has been reported[2] that an improvement in the properties of certain clays in Wisconsin was obtained by the addition of small amounts of sodium carbonate.

DE-AIRING

Since its introduction in industry de-airing has come into wide use. The principle of evacuating clay in the plastic state had been known for years but it had never been successfully applied on a commercial scale. Its popularity, however, has been due mainly to the decided benefits it imparts to the working behaviour of clays in the forming process.

During the early stages of the application of de-airing to industrial extrusion machines, it was reported[3] as giving the following advantages:

1. Great improvement in the working properties of all clays on which it was tried.
2. Entire prevention of blistering in the extruded column.
3. Increased plastic strength both in tension and compression.
4. Increased dry transverse strength.
5. Decreased fired absorption and apparent porosity.
6. Increased fired transverse strength.
7. Lamination almost avoided.

Although experience has proved that most of these benefits are attainable by evacuation, it has been shown that de-airing is not a cure-all, and that all clays do not behave the same way to it. It must be used with discretion. In some cases it has caused drying troubles, in others, firing difficulties. It is also still difficult to say to what extent de-airing corrects lamination, although it does permit easier die adjustments.

Plate III illustrates one type of industrial auger machine equipped for de-airing. At the front of the pug-mill (A) is a die through which the tempered clay is forced into the vacuum chamber (B) where the air that had been included in the clay mass during the tempering process is withdrawn. The clay itself forms the seal at the entrance of the vacuum chamber. As the clay is emitted from this die into the vacuum chamber, revolving blades cut the clay into shreds suitable for de-airing. The shreds fall on to the augers which force the clay through the forming die (C), the compressed clay in which seals this end of the vacuum system. Tempered clay cannot be de-aired in bulk form, it must be shredded first into pieces not exceeding one inch in diameter. In some machines the shredding is accomplished by forcing the tempered clay through orifices of suitable size, instead of cutting the shreds. Experience has shown that a vacuum of at least 27 inches of mercury is required in order to realize the benefits of de-airing.

[1] Henry, E. C.: Ceramic Age, 21, 43 (1933).
[2] Unpublished paper on an investigation carried out at the University of Wisconsin.
[3] Everhart, J. O.: Ohio State Experiment Station, Bulletin No. 74.

CLAYS OR SHALES SELECTED FOR INVESTIGATION

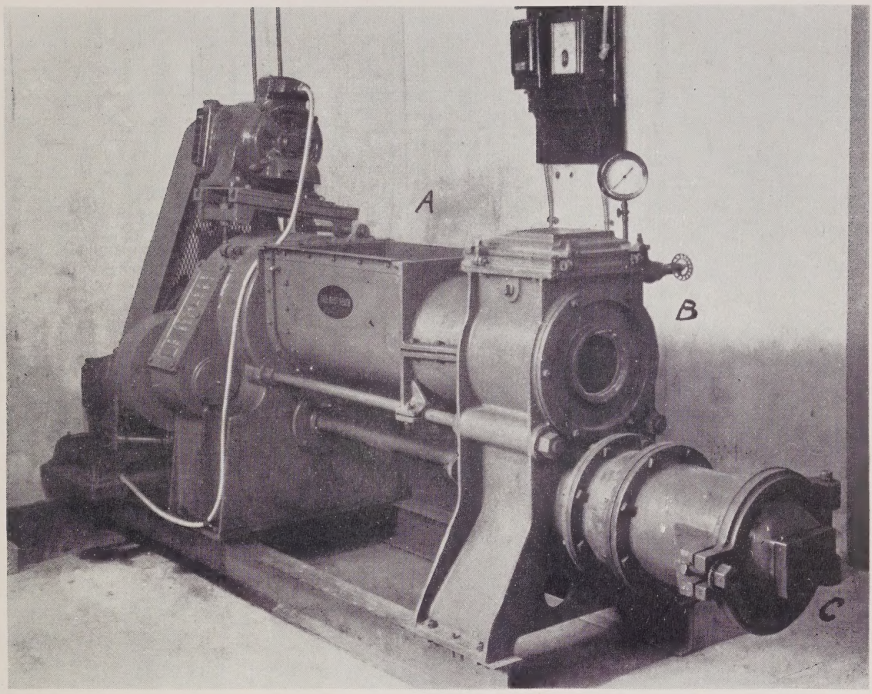
Shale No. 1. This material is a hard, highly calcareous shale, which has been used for a number of years at one of the large brick plants in Quebec for the production of common and face brick by the stiff plastic process. It does not readily slake in water, it develops little plasticity after tempering, and in firing retains a high percentage absorption almost to its overfiring temperature.

An experiment with the fired individual grains showed that an appreciable porosity is developed in the grains (owing to decomposition of lime carbonate). The average absorption of several small individual grains, fired to cone 06 (1841° C.) was found to be 5·23 per cent. After firing, therefore, there are two forms of pore in ware made from this shale; that developed in the individual grains by the decomposition of lime carbonate, and the interstices between grains. In order to test whether reduction in the pores of the second class might be accomplished by grading the grain sizes, an investigation was conducted in which the proportions of coarse, intermediate, and fine grains were varied and the effect on strength and absorption was measured. The results are given in Table V.

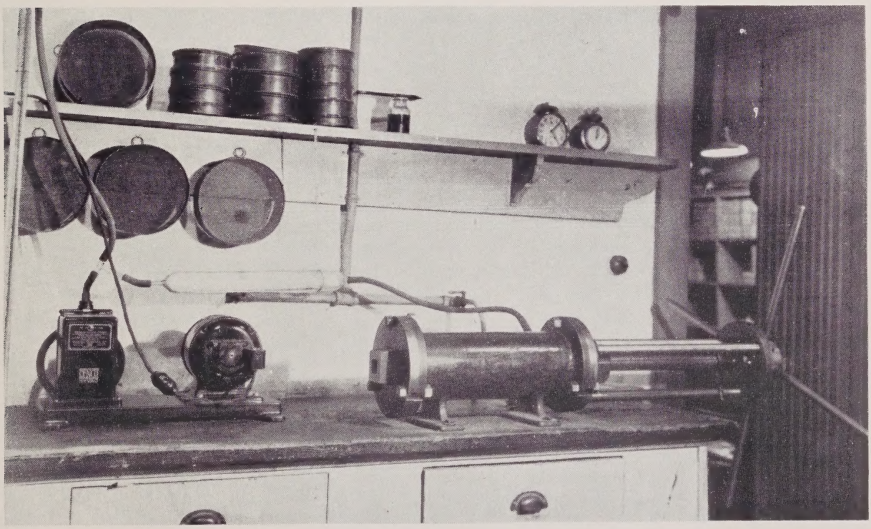
TABLE V

Ratio of grain sizes			Transverse strength modulus of rupture, lb. /sq. inch			Absorption, per cent		
−12+20	−20+65	−150	Dried at 85° C.	Cone 06	Cone 03	Cone 06	Cone 03	Cone 1
50	30	20	200	1010	1430	16·5	16·2	11·5
60	10	30	180	970	1100	16·4	15·8	12·0
60	—	40	200	1060	1400	17·0	16·0	12·2
40	—	60	250	1308	1500	16·2	16·0	12·4
40	50	10	146	800	940	16·0	15·8	12·0
35	45	20	155	1010	1090	16·0	16·0	11·5
30	40	30	160	1050	1110	16·0	16·0	12·2
25	35	40	168	1200	1260	15·8	15·5	12·0
30	60	10	135	850	1170	16·0	15·9	13·0
25	55	20	145	1000	1050	15·7	15·5	12·4
20	50	30	180	1070	1120	15·7	15·6	11·5
15	45	40	200	1200	1400	15·6	15·5	10·2
25	65	10	138	1000	1130	16·2	16·0	11·8
20	60	20	154	1100	1320	16·2	15·6	12·3
15	55	30	178	1280	1440	16·0	15·8	12·6
10	50	40	210	1320	1460	16·0	15·5	12·0

Although this study was not exhaustive it covered a sufficient range of variation in the proportion of grain sizes to show little hope for reducing absorption by grading. Some improvement in dry strength is obtainable



A. Small type of de-airing machine, convenient for semi-commercial tests: A, pug mill; B, vacuum chamber; C, forming die.



B. Laboratory de-airing machine.

by controlling the proportion of coarse to fine grains, but it is not considered sufficient to justify the cost of control. The shale as ground at the plant (with the plus 10-mesh material removed) gave the following screen analysis:

Mesh size	Percentage
— 10 + 14	27·48
— 14 + 20	17·57
— 20 + 28	11·64
— 28 + 35	9·07
— 35 + 48	5·79
— 48 + 65	4·51
— 65 +100	3·78
—100 +150	3·09
—150 +200	2·76
—200	13·80
Total.....	99·49

The strength and absorption determined in shale ground to this grading of grain sizes compared favourably with the optimum proportion obtained by regulation. The shale as ground at the plant (with the plus 10-mesh material removed) was therefore used in all subsequent experiments.

Shale No. 2. This material is representative of the Queenston shale from the vicinity of Hamilton, Ont., used extensively in the production of red face brick. It has fairly good working properties, but is rather low in strength in the green and air-dried state. It fires to a good red colour.

Clay No. 3. This is a mixture of calcareous, rather silty clay beds from the vicinity of Ottawa that is used in the production of hollow building tile, drain tile, and common brick. It contains soluble salt, which causes the ware to be badly scummed. By mixing the highly plastic with the silty clays a good working raw material is obtainable.

Clay No. 4. This material is a mixture of a surface clay and a moderately plastic, calcareous shale that is utilized in southern Ontario for the production of hollow building tile. This mixture maintains a rather high porosity until fired to a point close to its overfiring temperature.

Clay No. 5. This is a soft, calcareous, moderately plastic surface clay from L'Islet County, P.Q., that has been used in the production of hollow building tile and drain tile.

PRELIMINARY INVESTIGATION

A preliminary investigation was made of the clays by studying the effect of a variety of treatments on their working properties, dry and transverse strength, and fired absorption. In all cases of chemical treatment several percentage additions were made in order to avoid missing optimum points. The percentage additions of all chemicals were kept within practical limits; in no case was a 3 per cent (on the basis of the weight of the clay) addition exceeded.

GENERAL RESULTS OF PRELIMINARY INVESTIGATION

Hydrochloric and sulphuric acids gave no improvement in any of the clays studied and in most cases reacted adversely.

Such salts as ferric chloride, sodium chloride, aluminium chloride, ferric sulphate, and other flocculating salts gave no improvement.

Sodium carbonate, in additions under one per cent improved workability, gave a substantial increase in dry transverse strength, an increase in fired transverse strength, and a slight reduction in fired absorption.

De-airing gave a substantial improvement in working properties, an increase in dry and fired transverse strength, and in some cases a slight decrease in fired absorption.

In the preliminary tests the only treatments that offered any promise were de-airing, and the addition of sodium carbonate. It was decided then, to investigate fully the effect of these two methods of treatment, and combinations of the two on the particular clays in question.

METHOD OF INVESTIGATION

The plastic behaviour of the various clays and changes resulting from treatments was studied by observations made on a column extruded through a one-inch die. The machine, illustrated in Plate IIIB, was designed so as to permit de-airing. In order to carry out de-airing in this type of extruding machine it was necessary to cut the clay (after tempering with water) into shreds one-half inch in diameter before placing it in the extrusion chamber. After extrusion the one-inch column was cut into test pieces 6 inches in length. Determinations of dry transverse strength were made on three test pieces (drying temperature was 65° C. in all cases). The rest were fired to different temperatures after which fired transverse strength and percentage absorption determinations were made.

RESULTS

Figure 11 presents graphically the effect of various additions of sodium carbonate on the dry transverse strength of the several clays. The dry transverse strength of the de-aired clays in the plastic state without the addition of sodium carbonate is also shown.

The curves in Figures 12 to 16 show the effect of additions of sodium carbonate and de-airing on the fired transverse strength and absorption of the various clays.

Shale No. 1. As shown by the curves (Figures 11 and 12) treatment of this clay with sodium carbonate gives a substantial increase in air-dried and fired transverse strength, and a small reduction in absorption. De-airing benefited working properties to a marked degree, but did not increase strength nor reduce absorption so much as the treatment with sodium carbonate.

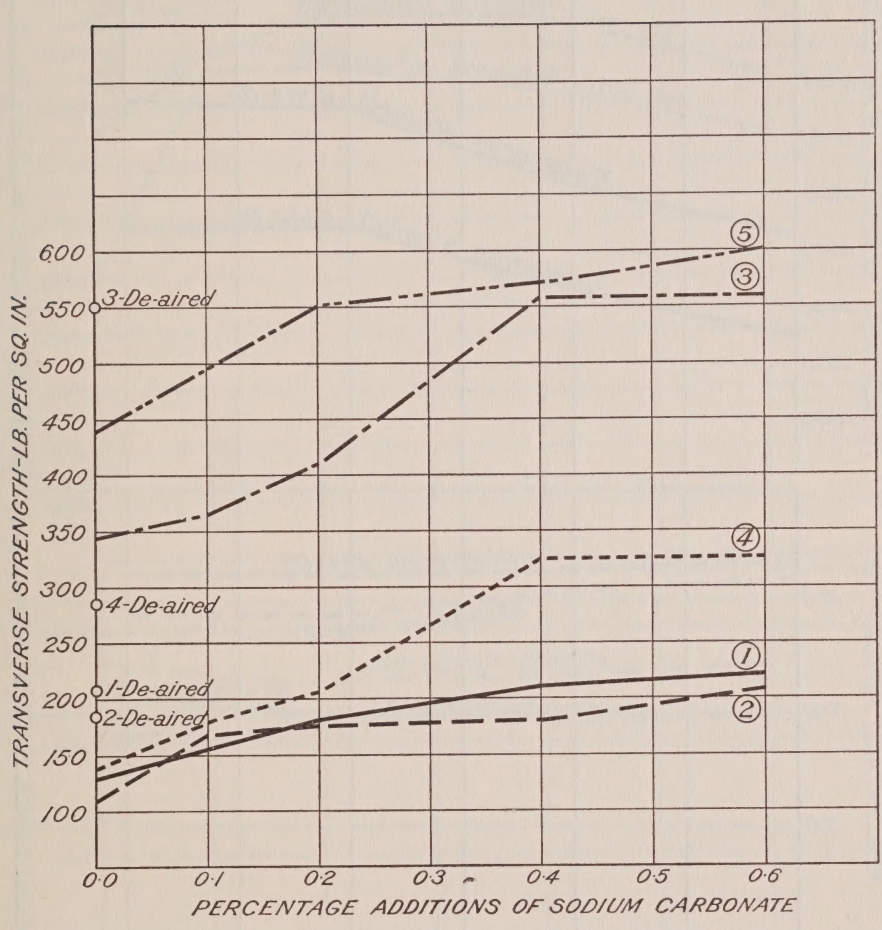


Figure 11. Effect of sodium carbonate and de-airing on dry transverse strength of clays investigated.

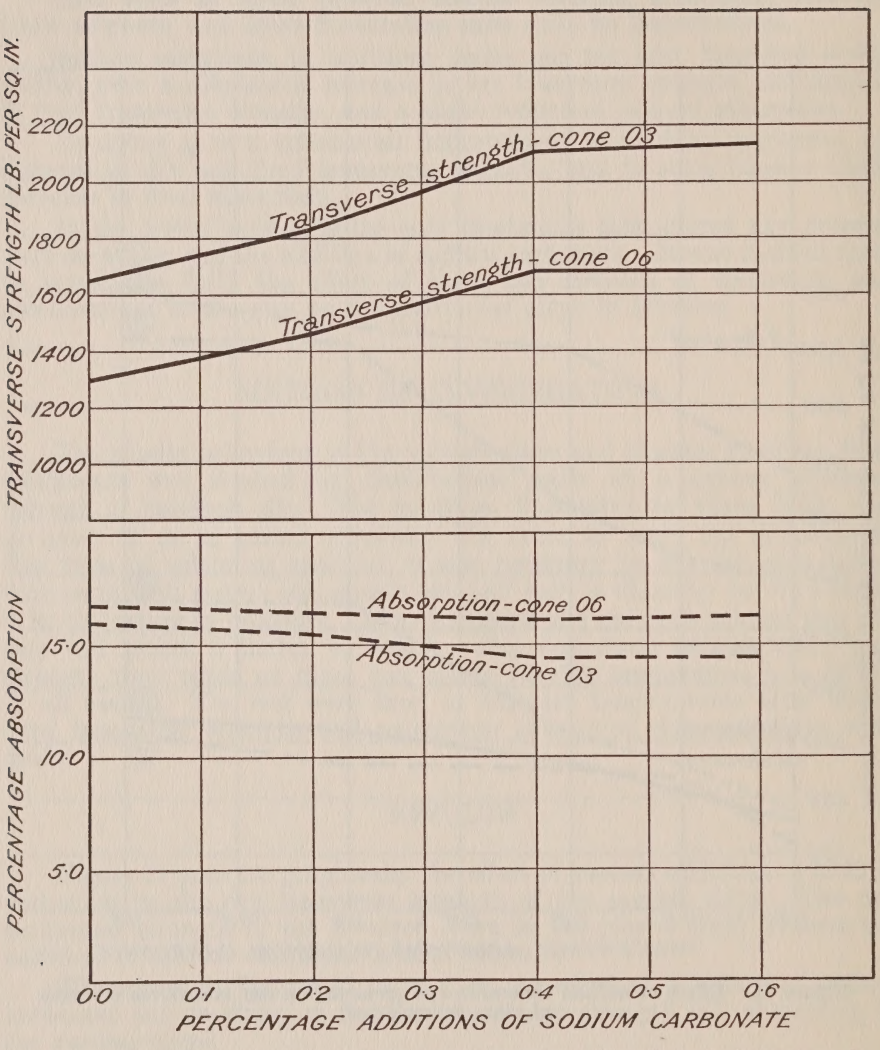


Figure 12. Effect of sodium carbonate on transverse strength and absorption of Shale No. 1 burned at Cone 03 and Cone 06.

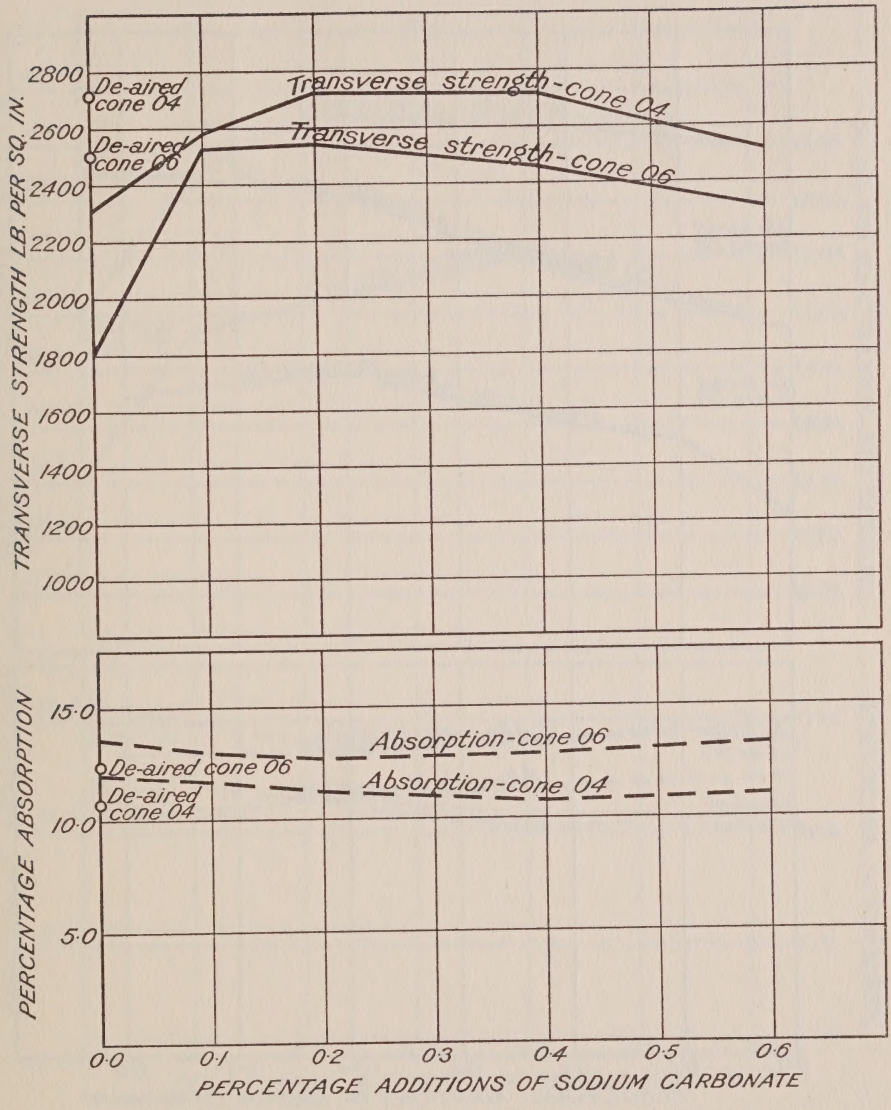


Figure 13. Effect of sodium carbonate on transverse strength and absorption of Shale No. 2 burned at Cone 04 and Cone 06.

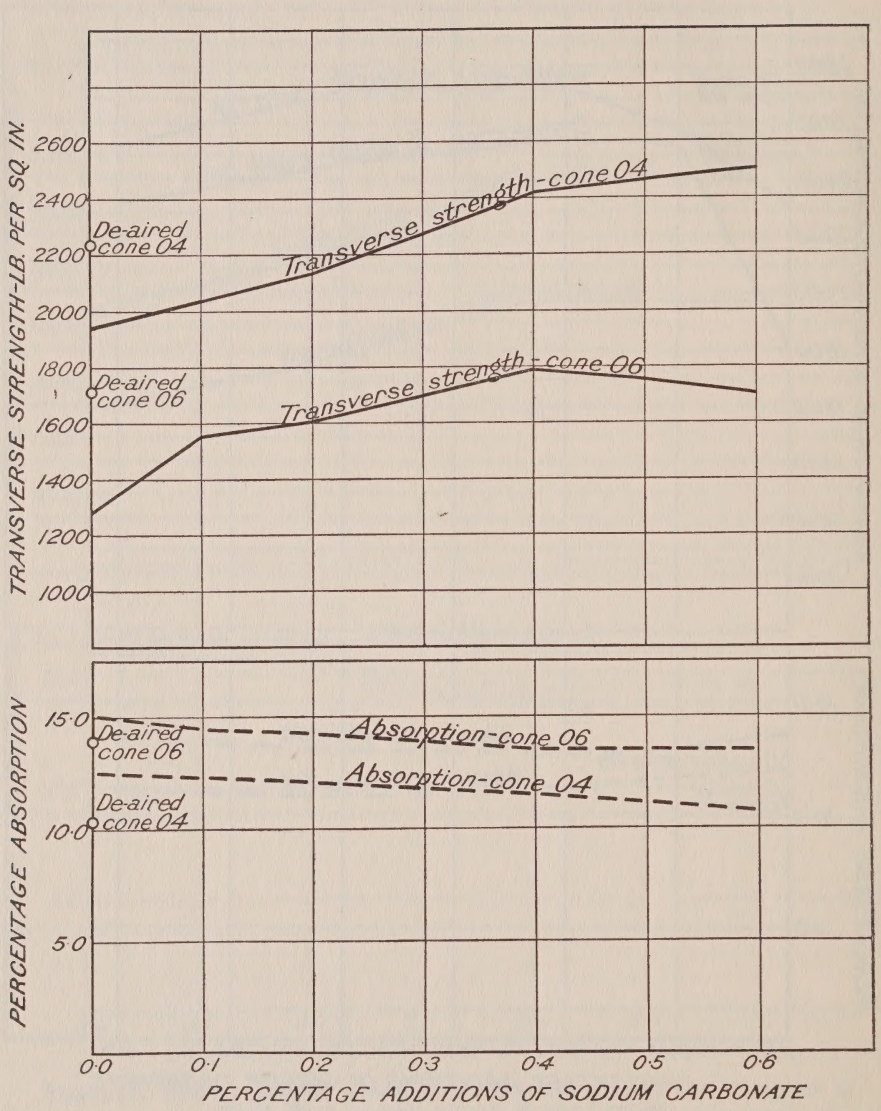


Figure 14. Effect of sodium carbonate on transverse strength and absorption of Clay No. 3 burned at Cone 04 and Cone 06.

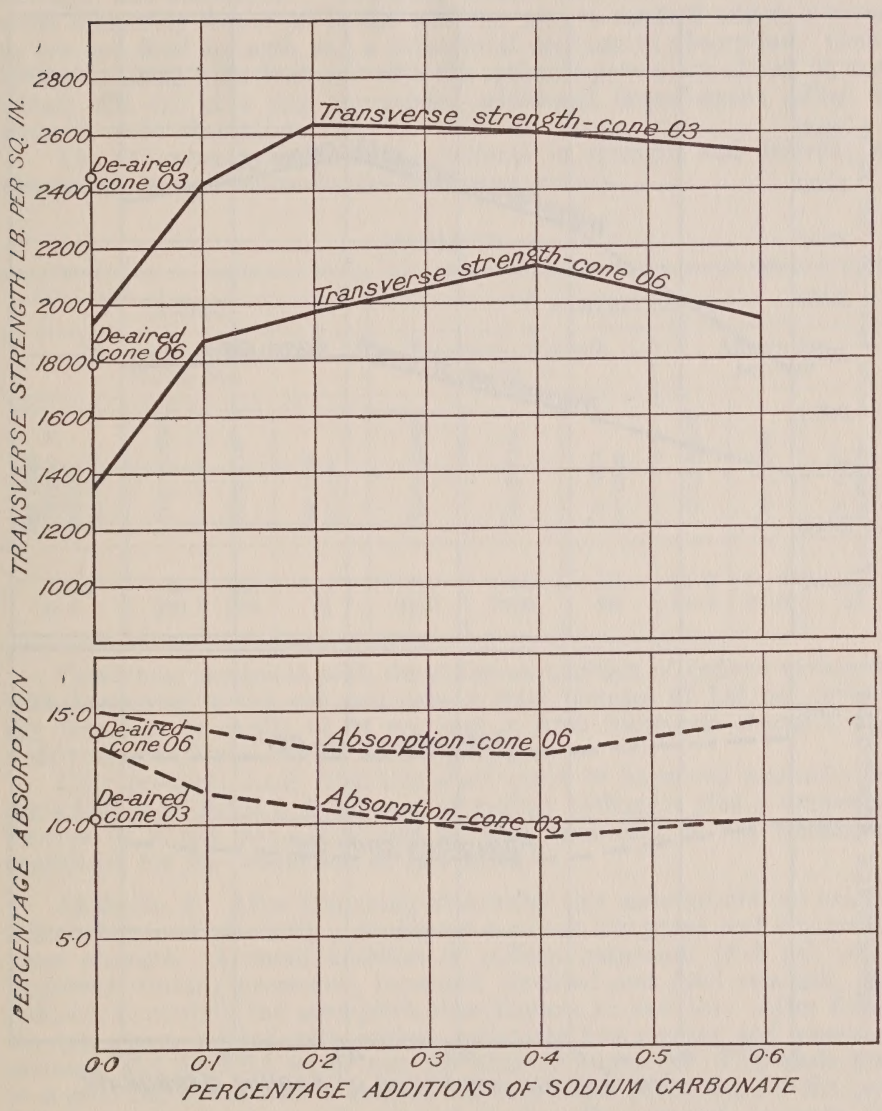


Figure 15. Effect of sodium carbonate on transverse strength and absorption of Clay No. 4 burned at Cone 03 and Cone 06.

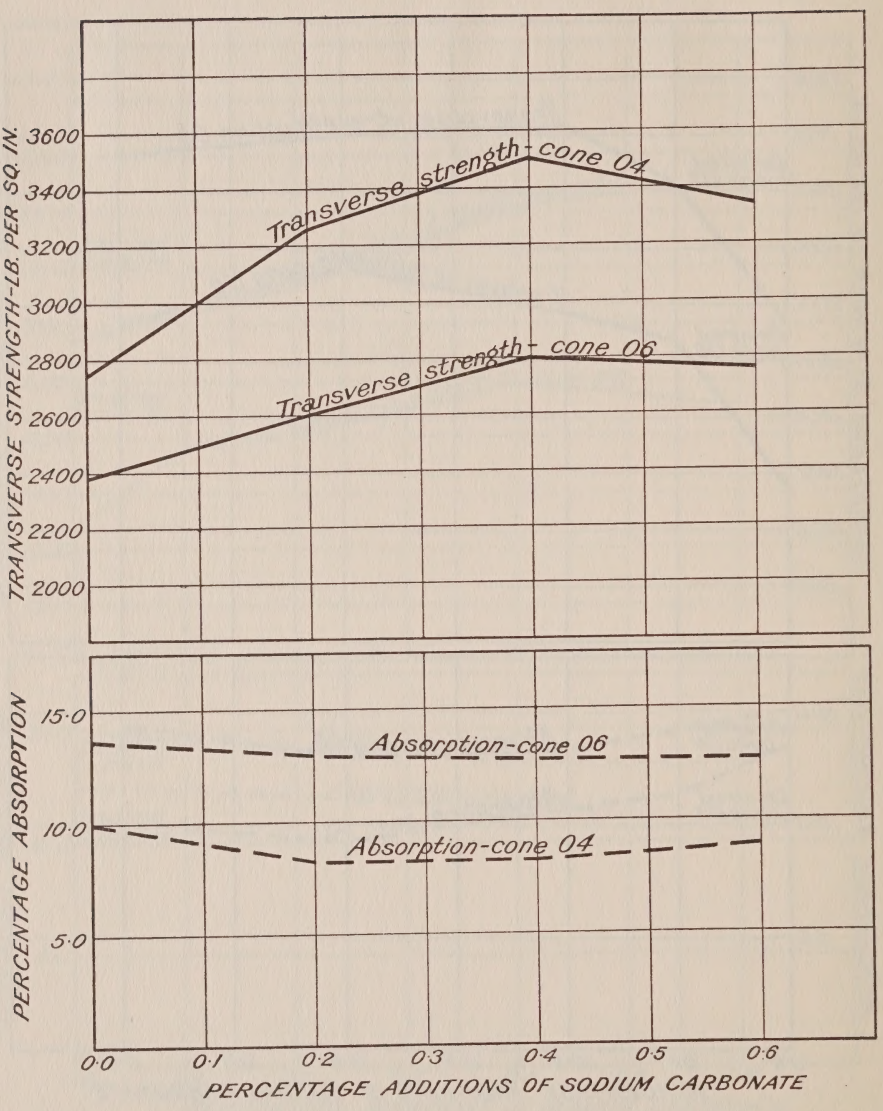


Figure 16. Effect of sodium carbonate on transverse strength and absorption of Clay No. 5 burned at Cone 04 and Cone 06.

In the case of this feebly plastic shale, tempering the untreated clay for a short period in a wet pan improved to some extent working properties, strength, and absorption. Combining sodium carbonate treatment with a short tempering treatment in the wet pan gave a marked added increase in dry and fired strength and a substantial decrease in absorption. Combining de-airing with treatment with the optimum percentage of sodium carbonate did not give any appreciable additional improvement either in strength or in absorption.

The following table gives the increase in strength and decrease in absorption, brought about by the tempering process.

TABLE VI

Air-dried				Fired to Cone 03					
	Transverse strength, lb./sq. in.			Transverse strength, lb./sq. in.			Absorption, per cent		
Per cent addition of sodium carbonate	Untempered	Tempered	Per cent increase	Untempered	Tempered	Per cent increase	Untempered	Tempered	Per cent decrease
None	130	190	46	1640	1800	10	16·0	14·8	7
0·4	260	290	11	2100	2700	28	14·5	12·6	13

Combining treatment with the optimum addition of sodium carbonate with tempering in the wet pan gave a total increase of 123 per cent in dry transverse strength, of 64 per cent in fired transverse strength, and a decrease of 27 per cent in fired absorption.

Clay products made from this shale could be improved markedly by the addition of about 0·4 per cent of sodium carbonate plus a tempering process in a wet pan. The cost of such treatment is not considered exorbitant for the production of face brick.

Shale No. 2. After tempering with water this material did not exhibit a high degree of plasticity. It showed a rather low green and dry transverse strength. A small addition of sodium carbonate (0·2 per cent) improved working properties, increased air-dried and fired strength, and reduced, somewhat, the absorption (See Figures 11 and 13). After firing, the test pieces treated with sodium carbonate had cleaner and smoother surfaces, and the fired colour was also slightly improved. This shale fires to a good red colour and in general has favourable properties for the production of clay products. In view of the benefits imparted, however, the use of a small amount of sodium carbonate is considered well worth while, particularly if the stiff-mud process of manufacture be employed.

Clay No. 3. This clay mixture responded favourably to the sodium carbonate treatment as is shown by the curves (Figures 11 and 14). The sodium carbonate also prevented the scum that ordinarily appeared on the

surface of ware made from this material. De-airing gave a much stronger and tougher extruded column, but as regards air-dried strength, fired strength, and absorption, sodium carbonate treatment compared favourably with de-airing.

Clay No. 4. Sodium carbonate gave a substantial increase in the dry and fired transverse strength of this clay. A small reduction in absorption was obtained by additions of from 0·2 to 0·4 per cent of sodium carbonate. (See Figures 11 and 15.)

Clay No. 5. Sodium carbonate in additions of from 0·2 to 0·4 per cent gave a large increase in the dry transverse strength of this clay (see curve, Figure 11), together with a substantial increase in fired transverse strength, and a small reduction in absorption (Figure 16). The clay is moderately plastic, but an improvement in working properties was noted in the clay treated with sodium carbonate; the extruded column was smoother, and a cleaner cut was made by the cutting wire.

SUMMARY

In the attempt to improve working properties, strength, and density, of all the chemicals tried, sodium carbonate was found to be the only one that benefited the clays or shales under investigation. Other sodium compounds such as trisodium phosphate and sodium hydroxide were not so effective as sodium carbonate and, being more expensive, were discarded.

In the case of these calcareous clays or shales, sodium carbonate was found (1) to improve working properties to some extent, (2) to increase greatly dry strength, (3) to increase greatly fired strength, and (4) to reduce slightly the absorption of the fired ware.

Sodium carbonate was also found to prevent scum and to impart a slightly improved colour and surface appearance.

When sodium carbonate is added some alteration of tempering water is necessary.

The effect of de-airing is much more pronounced than sodium carbonate treatment on working properties, but as regards dry strength, fired strength, and absorption, the two are comparable.

The sodium carbonate used was a commercial grade of soda ash (58 per cent of Na_2CO_3). An 0·4 per cent addition to clay or shale would cost about 45 cents per thousand brick. As the use of sodium carbonate usually obviates the necessity of adding barium carbonate to prevent scumming (or at least appreciably reduces the amount required) the cost of barium saved can be deducted.

Sodium carbonate being soluble is easily added to the tempering water.

CHAPTER V

IMPROVING THE FIRED COLOUR OF BRICK

In the production of structural clay products it is often desirable to obtain a good red colour, or flashed shades. With an appreciable content of lime a good clear-red fired colour is usually difficult and often impossible to obtain, because lime counteracts the red colouring effect of the iron minerals and the result is a colour that ranges from an off-shade of buff to "salmon." If a large amount of iron in extremely finely divided form is uniformly distributed, it is possible to obtain a good red colour in the presence of lime, provided the lime content be low and the iron content comparatively high. The better red-burning clays or shales from the vicinity of Toronto and Montreal are examples of this type of clay.

It has been found possible in some cases to improve the colour of red-burning clays by adding iron oxide, but if the clay contains a large amount of lime, as many of the Canadian glacial clays do, the bleaching power of the lime is so strong that even large additions of iron oxide fail to induce a good red colour.

Fabianic, working with a red-burning clay that analysed

	Per cent		Per cent
SiO_2	62·98	MgO	1·89
Al_2O_3	18·64	MnO	0·10
Fe_2O_3	5·26	Alkalis	4·85
CaO	1·69		

obtained some interesting results by adding various metal oxides. He reports:[1]

"A buff was obtained by the addition of 28 per cent of buff-burning clay, a fine deep red was secured by the addition of 3 per cent of Fe_2O_3, and a beautiful series of colours ranging from a dark yellow to an old ivory was obtained by additions of from 6 to 10 per cent of lime carbonate." He also obtained some interesting colour effects by adding titanium oxide in the form of rutile. By adding 3 to 8 per cent of rutile he obtained colours from an orange-yellow to old ivory.

Some plant operators may find it worth while to experiment with the oxides mentioned above, but if the lime content of their clay be high there is little hope of success.

GLAZING OF ROUGH-TEXTURED SURFACES

A suggested method of altering the face colour of brick, and one that offers an unlimited range of colours, is the glazing of the rough-textured surface of face brick.

"The glazing of face brick made from red-burning clays has always presented difficulties. In applying an impervious glaze to the ordinary

[1] Fabianic, W. F.: "Getting New Colour Effects on Face Brick"; Ceramic Age, Vol. 19, No. 3, p. 116 (March, 1932).

unvitrified face brick, a fit between glaze and body so that crazing would not develop could not be depended upon. By spraying a glaze or slip on to the roughened surface the glaze is broken up and all the difficulties of glaze fit are eliminated. In this way the glaze imparts colour without becoming an impervious glaze. A heavy glaze application masks the colour entirely while a thin application gives, with the body colour, a two-tone effect. Various effects can also be obtained from different methods of roughening the surface, that is, by using either deep scratch, rug, or mat surface."[1]

This method has been successfully used in recent years. The glaze is sprayed on the dried brick, the brick are set on the flat in the kiln, and fired under oxidizing conditions. The glazes are selected or adjusted so that the brick and glaze mature together.

Longenecker also reports that the slips developed by Montgomery and Tefft[2] have been tried and found to give good results. He lists the following advantages and disadvantages for slips and glazes.

(1) The slip costs less, pound for pound than the glaze.
(2) The slip will give less trouble from volatilization or any of the common physical defects.
(3) The slip is more likely to prove a durable coating when applied to unvitrified ware.
(4) The slips are dull and do not produce glare as does a bright glaze.
(5) The setting of slips is simpler as they do not run as do some fluid glazes.

The glazes have some advantages too:

(1) They use less colouring material than slips to obtain an equal colouring effect.
(2) They are impervious where a slip may be porous and become stained.

IMPROVING THE COLOUR OF SOFT-MUD BRICK BY THE ADDITION OF COLOURING AGENTS

Some success in improving the colour of sand mould brick has been attained by using mould sand in which are incorporated colouring agents. A most effective means of obtaining a mould sand with considerable colouring power is to use the brushings from foundry castings, which is a fine sand containing much iron oxide.

The mixing of flue dusts from metallurgical smelters with mould sand has also been experimented with with some success.

Experiments[3] have been made by adding a variety of colouring chemicals and colouring oxides to mould sands, but generally it has been found necessary to fire to cone 01 or higher to make the sand stick sufficiently tight so that it cannot be rubbed off.

Many of the chemicals, too, exhibit a decided tendency toward volatilization, which renders them ineffectual.

The use of the brushings from foundry castings provides a cheap and often effective means of colouring soft-mud brick. The admixture of some flue dusts is worthy of consideration as this also is an inexpensive source of supply. For the best results the brick should be fired in an oxidizing atmosphere, and, if possible, a temperature should be attained that will give some fluxing or sintering between body, sand, and colouring agent.

[1] Longenecker, H. L.: "Glazing Textured Brick with Colours"; Brick and Clay Record, 87, (3), 89 (1935).
[2] Montgomery, E. T., and Tefft, C. F.: Trans. Amer. Cer. Soc., Vol. 16, p. 144.
[3] Lobaugh, F. E.: "Colours for Sand Mould Brick," Brick and Clay Record, 90, (4), 227 (1937).

IMPROVING COLOUR AND SURFACE TEXTURE BY ENGOBING

The use of engobes to get certain desired colours and surface textures on roofing tiles is an old practice. In recent years the possibilities offered by the engobing method in the colouring of brick or tile have been receiving a great deal of attention in Europe, and considerable experimental work has been carried on to develop improved engobes.[1] A simple method of engobing that is applicable to almost any kind of clay was recently discovered and it is considered of sufficient general interest to brick and tile manufacturers in Canada to quote in detail the description of the process given in Dr. Felix Singer's article, to which reference has already been made. This method, which is ostensibly a revival of the ancient "terra sigillata" used by the Romans, was discovered by Dr. Schumann.[2] The procedure is as follows:

Clay burning red, white, or any other colour, or artificially stained clay, is suspended in water and a small quantity of liquefying electrolytes added. Then follows a thorough dilution of this clay slip, so that a specific gravity of 1·2 or less is attained. This dilution is best obtained by the addition of ice. The suspension is then separated from sediment; the comparatively thin slurry thus obtained is the actual "terra sigillata" engobe with which the ware in question is to be coated—in practically the usual way—either in the plastic, leather-hard, stiff or white dry state, by pouring, spraying or similar means, to be fired normally after drying.

It is important when carrying out this process, to regulate the suspension to a specific gravity of 1·2 at the most, and to employ a very small quantity of electrolytes, alkalis, alkali carbonates, sodium silicate, etc. (the Romans probably used wood ashes, i.e. potassium carbonate). It may be necessary to add protective colloids, such as high molecular organic substances like humic acid, tannin, etc. Further, it is important that the suspension with the very low specific gravity is freed from the coarse particles which may be distributed in the slip. Therefore the suspension is allowed to stand for some time, or subjected to a centrifugal process.

The correct preparation of the suspension can be investigated by pouring some on to a glass plate. If rightly regulated it should dry in a practically transparent film with no solid particles to be seen with the eye. A further criterion for the correct suspension is as follows: It should show no sediment after standing a long time, and it should be able to be concentrated by evaporation, etc., without becoming dull again, or, if it does so, without showing signs of precipitation.

The presence of electrolyte additions, and sometimes also of protective colloids, is essential for obtaining the right consistency of the slurry, because the particles of clay are thus distributed in a colloid fineness. Such slips are extremely watery, durable and transportable, and they can be used immediately as engobes for pouring or spraying of the goods. For purposes of transport or other special cases, they can be thickened by evaporation or other concentration methods.

It is also possible, according to Dr. Schumann's process, to make coloured terra sigillata engobes in a certain way. For this purpose colloidal metallic oxides such as iron oxide, cobalt oxide and copper oxide, are added to the slip during or after preparation.

A special advantage is to have the body and engobe made from the same clay, when, for example, the clay to be used for producing the goods is subjected to the washing process described above. Then the finest constituents remaining in the suspension are used for the preparation of the overcoating, and the sediment added to the main body. Iron-containing and also manganese-containing and white-burning clays can be worked up and used.

The firing of the goods coated with the described slip can be done in any ceramic kiln. The overcoating neither fuses nor sticks to the other ware, and this is the greatest advantage of these terra sigillata engobes over other glazes which are also dense.

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[1] Singer, Felix: "Modern Methods of Brick and Tile Colouring;" British Clay Worker, Feb. 389 (1938).

[2] German Patent No. 626112. British patent applied for.